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Atty. Dkt. No. 056859-0190

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Arvind SINHA et al.

Title: A SINGLE-STEP SIMPLE AND ECONOMICAL PROCESS FOR THE PREPARATION OF NANOSIZED ACICULAR MAGNETIC IRON OXIDE PARTICLES OF MAGHEMITE PHASE

Appl. No.: 10/694,394

Filing Date: 10/28/2003

Examiner: Unassigned

Art Unit: Unassigned

CLAIM FOR CONVENTION PRIORITY

Commissioner for Patents
PO Box 1450
Alexandria, Virginia 22313-1450

Sir:

The benefit of the filing date of the following prior foreign application filed in the following foreign country is hereby requested, and the right of priority provided in 35 U.S.C. § 119 is hereby claimed.

In support of this claim, filed herewith is a certified copy of said original foreign application:

- Indian Patent Application No. 1094/DEL/2002 filed 10/30/2002.

Respectfully submitted,

Date: March 5, 2004

By Michael D. Kaminski

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Customer Number: 22428
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Michael D. Kaminski
Attorney for Applicant
Registration No. 32,904

सत्यमेव जयते

INTELLECTUAL PROPERTY **INDIA**

GOVERNMENT OF INDIA
MINISTRY OF COMMERCE & INDUSTRY,
PATENT OFFICE, DELHI BRANCH,
W - 5, WEST PATEL NAGAR,
NEW DELHI - 110 008.

I, the undersigned being an officer duly authorized in accordance with the provision of the Patent Act, 1970 hereby certify that annexed hereto is the true copy of the ***Application*** *and* ***Complete Specification*** *filed in connection with Application for Patent No.* ***1094/Del/2002*** *dated* ***30th October 2002.***

Witness my hand this 7th day of January 2004.

(S.K. PANGASA)
Assistant Controller of Patents & Designs

1094 DEL 02

30/10/2002

FORM 1

THE PATENT ACT, 1970
(39 of 1970)

APPLICATION FOR GRANT OF PATENT
(See Section 5(2), 7, 54 and 135 and rule 33A)

1. We, COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Rafi Marg, New Delhi-110001, India, an Indian registered body incorporated under the Registration of Societies Act (Act XXI of 1860),
2. Hereby declare:
(a) that we are in procession of an invention titled: "A process for the preparation of nanosized acicular magnetic iron oxide in magnetic field by biomimetic route"

(b) that the ~~Provisional~~/Complete specification relating to this invention is filed with this application;
(c) that there is no lawful ground of objection to the grant of patent to us;

3. further declare that the inventor(s) for the said invention is/are:

Arvind Sinha, Jui Chakraborty and Venkatesh Rao
ALL OF NATIONAL METALLURGICAL LABORATORY, JAMSHEDPUR, JHARKHAND, INDIA,
ALL ARE INDIAN CITIZEN

ORIGINAL

4. We, claim the priority from the application(s) filed in convention countries, particulars of which are as follows: NOT APPLICABLE

5. We state that the said invention is an improvement in or modification of the invention, the particulars of which are as follows and of which we are the applicant:
(a) Patent application no. :
(b) Patent application date :

6. We state that the application is divided out of our application, the particulars of which are given below and pray that this application deemed to have been filed on .....under section 16 of the Act.
(a) Patent application no.
(b) Date of filing provisional and/or complete specification ..... and .....

7. That we are the assignee of the true and first inventor(s)

8. That our address for service in India is as follows:-

Head, IPM Division, CSIR
INSDOC Building, 14, Satsang Vihar Marg,
New Delhi-110067

Phone: 696 2560, 696 8819, Fax: 696 8819

PTO

9. Following declaration was given by the Inventor(s):

I/We the true and first inventor(s) for this invention declare that the applicants herein is / are my / our assignee:

Dated this 30th day of October, ~~19~~2002

Name (in full with expanded initials)	Signature of the true and first inventor(s)
Arvind Sinha	Arvind Sinha
Jui Chakraborty	Jui Chakraborty
Venkatesh Rao	Venkatesh Rao

10. That to the best of our knowledge, information and belief the fact and matters selected herein are correct and that there is no lawful ground of objection to grant of patent to us on this application.

11. Following are the attachment with the application:
- (a) ~~Provisional~~ / Complete specification (3 copies).
- (b) Drawings (3 copies).
- (c) Priority document(s).
- (d) Statement and Undertaking on FORM-3.
- (e) Power of authority.
- (f) Fee Rs. ~~5000~~ 865352 in Cheque no. : 24/9/02 dated: 24/9/02 on State Bank of India, New Delhi Main Branch, Parliament Street, New Delhi-110001

We request that a patent may be granted to us for the said invention.

Dated this 30th day of October, ~~19~~2002

( )
SCIENTIST
Intellectual Property Management Division)
Council of Scientific and Industrial Research

To,
The Controller of Patents,
The Patent Office, New Delhi

NF 430-02

1094 DEL 02

FORM - 2
The Patents Act -1970
(39 of 1970)

30 OCT 2002

COMPLETE SPECIFICATION
(See section -10)

A PROCESS FOR THE PREPARATION OF NANOSIZED ACICULAR MAGNETIC IRON OXIDE IN MAGNETIC FIELD BY BIOMIMETIC ROUTE

ORIGINAL

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH
Rafi Marg, New Delhi - 110 001, India
An Indian registered body incorporated under the registration of Societies Act
(Act. XXI of 1860)

The following specification particularly describes the nature of the invention and the manner in which it is to be performed

This invention relates to a process for the preparation of nanosized acicular magnetic iron oxide in magnetic field by biomimetic route. This invention particularly relates to a single step biomimetic route for the preparation of nanosized acicular maghemite in magnetic field which is used for the magnetic memory storage. The nanosized acicular maghemite particles, a form of iron oxide, in the range of 300-350 nm in size will be suitable as a particulate medium for perpendicular magnetic recording in general and in audio / video tapes in particular.

Magnetic pigments have been used in electronic recording devices since the late 1940's. The moderate cost of production and the chemical stability make maghemite the principal magnetic pigment for the purpose. Though magnetite, another iron oxide, displays high magnetization and coercivity, it is less suitable for recording devices due to its magnetic instability.

Much of the art of creating a good magnetic medium lies in the preparation method of the pigment. New materials for magnetic recording may be limited by the superparamagnetic relaxation produced by the small size of the particle (<30 nm). Particle shape is also an important factor as it determines the shape anisotropy and then the coercive field value. For longitudinal magnetic recording, particles must show acicular shape.

The conventional route of synthesis of acicular maghemite particles through oxyhydroxide method is multistep and complicated. It becomes further difficult to produce nanosized maghemite particles through this process as a result of a poor control over the growth kinetics. In another method, oxidation of magnetite particles result in formation of either cubic or irregular maghemite particles. The crystals of

<300 nm size are completely transformed to the maghemite phase at 200-250°C, whearas, for larger crystals, the oxidation is incomplete. The process being single step, however, involves a relatively higher temperature to produce maghemite particles of negligible aspect ratio.

Reference may be made to R.Robl, Anges Chem., 1958, *70*, pp. 367, wherein oxidation of ferrous sulphate solution was carried out with potassium nitrate followed by which the solution was heated to 60-80°C and added sodium hydroxide solution slowly with continuous stirring. The black precipitate formed was washed and dried and was heated to 250°C for 30 minutes leading to the formation of maghemite particles.

Reference may be made to R.M.Taylor and U. Schwertman, Clay Min., 1974, *10*, pp. 299-310, wherein equal volumes of ferrous and ferric salt solutions were mixed and was heated to 40°C. To this was added the requisite amount of sodium hydroxide when a black precipitate was formed. This was filtered, washed, dried in air when the precipitate turned dark brown and was identified to be maghemite.

Reference may be made to Y.Maeda, The Electronics & Tele-Communication Laboratories, NNT, E.C.L Techn. Publ., 1978, *179*, pp. 1-7 wherein a solution of ferrous sulphate with sodium hydroxide leads to the formation of ferrous hydroxide. This was oxidized rapidly by passing air for 45 minutes with stirring which results in the formation of ferrous oxyhydroxide. This was again mixed with a solution of ferrous sulphate and iron wire was placed in the solution followed by which 8-10 litre air / minute was passed for 48 hours while maintaining the temperature at 60°C. The ferrous oxyhydroxide was separated from the solution, washed and dried at 130°C and

heated with hydrogen in a stirred autoclave at 440°C until the magnetite content was 23.8 %. After cooling to 250°C, air was passed in until the ferrous salt was absent.

Reference may be made to R.D.Gautam and Madan Rao, Mater. Res. Bull., 1982, *17*, pp. 443, wherein lepidocrocite is treated with pyridine and carefully oxidized for a long period for complete conversion to nanosized maghemite particles.

Reference may be made to G. Ennas, G.Marongiu, A.Musinu, A.Falqui, P. Ballirano and Camintin, J. Mater. Res., 1999, *14*, pp.1570, wherein, through a wet chemical synthesis of successive hydrolysis, oxidation and dehydration of ferrous chloride was perfomed to obtain maghemite particles as small as 5 nm.

Reference may be made to G.V.Gopal Reddy, Sheela Kalyana and S.V.Manorama, Int. J. Inorg. Mater., 2000, *2*, pp.301, wherein synthesis of maghemite for sensor application through a novel technique of combustion of ferric salts with hydrazine hydrate has been carried out.

Reference may be made to K.E.Gonsalves, H.Li, and P.Santiago, J. Mater. Sci., 2001, *36*, pp. 2461, wherein lepidocrocite has been converted into maghemite by a colloidal process in which the particles could be readily dispersed into an organic solvent. The as- prepared acicular maghemite nanorod-ethanol dispersion containing 0.005 g nanorods was centrifuged, the supernatant solvent was decanted followed by the addition of 8.3 g of 6 wt % PMMA (polymethyl methacrylate) solution, and the mixture was sonicated for several hours in an ice-water cooling bath. The concentration of the magnetic maghemite nanorods was about 1 % relative to the PMMA.

All the above processes are expensive and involve complicated steps.

Moreover, the maghemite particles produced have poor crystallinity, mixed phase, random variation in morphology, low aspect ratio and magnetically induced agglomeration. The above limitations reduce the applicability of the magnetic pigments in the field of magnetic information storage.

The main object of the present invention is to provide a process for the preparation of nanosized acicular magnetic iron oxide in magnetic field by biomimetic route which obviates the drawbacks as detailed above.

Another object of the present invention is to provide a single step process for preparation of nanosized acicular maghemite particles induced by magnetic field following a room temperature biomimetic process.

Since the evolution of life, synthesis of nano- and microsized inorganic particles is observed in nature. Under the control of a biopolymeric matrix, the *in situ* synthesis of these inorganic minerals exhibit a precise control over their nucleation and growth which result in precipitation of agglomeration free particles. Our teeth, bone, shells are some of the common products of biomineralisation in nature.

In the process of present invention a method has been developed for *in situ* precipitation of uniformly acicular, single phase maghemite particles having a high aspect ratio in a preorganised water soluble polymer matrix, polyvinyl alcohol, held at room temperature and atmospheric pressure. The method produced maghemite particles in the size range of 300-350 nm having uniform morphology, orientation and a high aspect ratio.

Under the optimum conditions of temperature, concentration, pH and a specific relative volumetric ratio, the underlying polymeric matrix provides a

regularly arranged and uniformly distributed reaction as well as nucleation sites in the self assembled polymeric network formed as a result of gelation. An optimum external magnetic field not only exerts a high degree of control over the growth epitaxy and orientation of the particles immobilized by the preorganized matrix but also induces the nucleation of maghemite phase having tetragonal unit cell instead of magnetite phase with cubic unit cell. Moreover, the polymer matrix anisotropy also provides a specific orientation during the particle growth.

Accordingly, the present invention provides a process for the preparation of nanosized acicular magnetic iron oxide in magnetic field by biomimetic route which comprises:

i.) mixing polyvinyl alcohol of strength ranging between 0.1-0.6% and iron salt solution of strength ranging between 0.1-0.15 % in a volumetric ratio ranging between 3:1 to 5:2 at a pH in the range of 2-5 and stirring for about 20 minutes by a magnetic stirrer,

ii.) heating the resultant solution at a temperature in the range of 30°C-60°C for about 24 hours in an oven under nitrogen atmosphere to obtain an iron ion loaded polymer gel,

iii.) soaking the above said polymer gel for a period ranging from 4-6 minutes into sodium hydroxide solution of strength ranging from 2-2.5 M, at a temperature ranging from 30°C-50°C under an external magnetic field ranging from 800-1500 Gauss,

iv.) washing the above soaked polymer gel with deionised water, to remove the sodium chloride salt and drying at a temperature ranging between 30°C-

60°C in an oven under nitrogen atmosphere for about 24 hours,

v.) recovering the uniformly acicular maghemite particles from the dried polymer gel by known method.

In an embodiment of the present invention, the iron salt solution may be prepared by dissolving ferric chloride and ferrous chloride salt in the ratio of 2:1 to 4:3 in de-ionised water.

In another embodiment of the present invention, the chemicals used may be of analytical grade.

By the process of the present invention, single phase, agglomeration free, oriented acicular maghemite particles in the size range of 300-350 nm with a high aspect ratio is produced.

The novelty of the present route lies in the single step biomimetic synthesis of monodispersed, high aspect ratio maghemite particles in presence of an applied magnetic field. Magnetic field, an external stimulus in this process pertaining to the nucleation of maghemite instead of magnetite, also induces directional growth leading to anisotropy.

In the present invention based on the principle of biomimetics, under an external stimuli, the microenvironment of the polymer matrix characterized by a regular arrangement of functional sites leads to an uniformly epitaxial growth of maghemite particles in a preferred crystallographic orientation induced by an optimum external magnetic field. The magnetic field is supposed to provide the necessary activation energy for the nucleation of the maghemite phase.

The following examples are given by way of illustration and should not be

construed to limit the scope of the present invention.

Example-1

60 ml of 0.5 % polyvinyl alcohol solution was mixed with 15 ml of 0.144 M iron salt solution in the volumetric ratio of 4:1 by continuous stirring using a magnetic stirrer. The pH of the solution was maintained at 3. The resulting solution was poured into a Petridish and subjected to gel formation in an oven at 40°C under nitrogen atmosphere for 24 hours. Next, the dried yellow thin film was soaked for a period of 2 hours in 2.05 M sodium hydroxide solution taken in a beaker and heated to 40°C, following which the colour of the film changed from yellow to black.This was washed 4-5 times with deionised water and dried in the same oven at 50°C under nitrogen atmosphere for 24 hours. The film was structurally characterized by X-ray diffraction, scanning electron microscopy and transmission electron microscopy. The analysis of the results obtained confirmed the formation of single phase, monodispersed and regularly oriented magnetite particles having cuboid, spheroid or cubooctahedral geometry.The particle size in this case was observed to be in the order of 80-100 nm, showing agglomeration to a certain extent. The recovery of these iron oxide particles were close to 100%.

Example-2

60 ml of 0.5 % polyvinyl alcohol solution was mixed with 15 ml of 0.144 M iron salt solution in the volumetric ratio of 4:1 by continuous stirring using a magnetic stirrer. The pH of the solution was maintained at 3. The resulting solution was poured into a Petridish and subjected to gel formation in an oven at 40°C under nitrogen atmosphere for 24 hours. Next, the dried yellow thin film was soaked under an

applied magnetic field of 890 Gauss for 5 minutes in 2.05 M sodium hydroxide solution taken in a beaker and heated to 40°C, following which the colour of the film changed from yellow to dark brown. The magnetic field was removed, the sample taken out and washed with deionised water 4-5 times and dried in the same oven under nitrogen atmosphere at 50°C for 24 hours. Next, the film was structurally characterized by X-ray diffraction, scanning electron microscopy and transmission electron microscopy. The analysis of the data indicated the presence of both the magnetite and the maghemite phases with a low particle density / unit area and almost without any agglomeration. The maghemite particles were oriented, having acicular morphology with a medium aspect ratio and were in the size range of 200-300 nm. The magnetite particles have irregular, spheroid or cubooctahedral geometry and were in the size range of 100-200 nm. The recovery of the maghemite particles were close to 70% whereas the recovery of the magnetite particles were close to 30%.

Example-3

60 ml of 0.5 % polyvinyl alcohol solution was mixed with 15 ml of 0.144 M iron salt solution in the volumetric ratio of 4:1 by continuous stirring using a magnetic stirrer. The pH of the solution was maintained at 3. The resulting solution was poured into a Petridish and subjected to gel formation in an oven at 40°C under nitrogen atmosphere for 24 hours. Next, the dried yellow thin film was soaked under an applied magnetic field of 1000 Gauss for 5 minutes in 2.05 M sodium hydroxide solution taken in a beaker and heated to 40°C, following which the colour of the film changed from yellow to dark brown. The magnetic field was removed, the sample taken out and washed with deionised water 4-5 times and dried in an oven under

nitrogen atmosphere at 50°C for 24 hours. Next, the film was structurally characterized by X-ray diffraction, scanning electron microscopy and transmission electron microscopy. The analysis of the data indicated the presence of single phase maghemite particles having a high particle density / unit area but with a mixed geometry of acicular (in the size range of 250-300 nm), spindle shaped and spheroid particles (in the size range of 50-100 nm). The particles in general were oriented, agglomeration free and the acicular maghemite particles have a high aspect ratio. The recovery of these iron oxide particles were close to 100%

Example-4

60 ml of 0.5 % polyvinyl alcohol solution was mixed with 15 ml of 0.144 M iron salt solution in the volumetric ratio of 4:1 by continuous stirring using a magnetic stirrer. The pH of the solution was maintained at 3. The resulting solution was poured into a Petridish and subjected to gel formation in an oven at 40°C under nitrogen atmosphere for 24 hours. Next, the dried yellow thin film was soaked under an applied magnetic field of 1175 Gauss for 5 minutes in 2.05 M sodium hydroxide solution taken in a beaker and heated to 40°C, following which the colour of the film changed from yellow to dark brown. The magnetic field was removed, the sample taken out and washed with deionised water 4-5 times and dried in an oven under nitrogen atmosphere at 50°C for 24 hours. Next, the film was structurally characterized by X-ray diffraction, scanning electron microscopy and transmission electron microscopy. The analysis of the data indicated the presence of single phase, monodispersed maghemite particles in the size range of 300-350 nm having oriented, acicular morphology with a very high aspect ratio and a high particle density / unit

area. The particles were completely agglomeration free.The recovery of these iron oxide particles were close to 100%.

Keeping other reaction parameters constant, the rate of reaction in any process depends largely on the orientation of the reacting molecules for an effective collision to overcome the energy barrier for the forward reaction. In the present case, the precipitated iron oxide particles being magnetic, the applied external magnetic field confers a high degree of orientation in the colliding molecules to increase the probability of the effective collisions for a successful chemical transformation as has been referred in the Arrhenius equation for the rate of reaction. As evident from the present experimental results, an optimum external magnetic field provides the necessary threshold energy (activation energy) and increases the frequency of the effective collisions greatly for the nucleation and precipitation of the maghemite particles. As observed, a lower field results in an incomplete chemical transformation resulting in mixed produets leading to precipitation of both magnetite and maghemite phases or a mixed geometry of acicular as well as spheroid and cubooctahedral particles.

The main advantages of the present invention are:

i.) The invention provides a room temperature single step process for the preparation of nanosized uniformly acicular maghemite particles with a high aspect ratio for application in the field of magnetic memory storage.

ii.) The invention leads to precipitation of agglomeration free maghemite particles having uniform shape and size.

We claim

1. A process for the preparation of nanosized acicular magnetic iron oxide in magnetic field by biomimetic route which comprises:

i.) mixing polyvinyl alcohol solution of strength ranging between 0.1-0.6 % and iron salt solution of strength ranging between 0.1-0.15 % in a volumetric ratio ranging between 3:1 to 5:2 at a pH in the range of 2-5 and stirring for about 20 minutes by a magnetic stirrer,

ii.) heating the resultant solution at a temperature in the range of 30°C-60°C for about 24 hours in an oven under nitrogen atmosphere to obtain an iron ion loaded polymer gel,

iii.) soaking the above said polymer gel for a period ranging from 4-6 minutes into sodium hydroxide solution of strength ranging between 2-2.5 M at a temperature ranging from 30°C-50°C under an external magnetic field ranging between 800-1500 Gauss,

iv.) washing the above soaked polymer gel with deionised water to remove the sodium chloride salt and drying at a temperature ranging between 30°C - 60°C in an oven under nitrogen atmosphere for about 24 hours,

v.) recovering the acicular maghemite particles from the dried polymer gel by known method to obtain the desired product.

2. A process as claimed in claim 1 wherein the iron salt solution used is prepared by dissolving ferric chloride and ferrous chloride salts in ratio of 2:1 to 4:3 in deionised water.

3. A process as claimed in claims 1-2 wherein the chemicals used in the present invention are of analytical grade.

4. A process for the preparation of nanosized acicular magnetic iron oxide in magnetic field by biomimetic route substantially as herein described with reference to the examples.

Dated this 30th day of October 2002

Scientist, IPMD